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PART II

RESEARCH ON SILICON AND PHOSPHORUS DERIVATIVES OF VARIOUS NITROGEN COMPOUNDS

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UNIVERSITY OF LONDON

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FOREWORD

This report was prepared by Birkbeck College, University of London, London, W. C. 1, England, on Air Force Contract Nr AF 61(052)-175 under Task Nr 73666, "New Synthetic Methods For Polymers And Fluids", of Project Nr 7023, "Research On Chemical Synthesis." The contract efforts were accomplished under the cognizance of the Nonmetallic Materials Division, Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. The technical work was directed by Dr. H. Rosenberg as project engineer.

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This technical report has been reviewed and is approved.

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Polymer Branch
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ABSTRACT

Trialkylphosphites or diphenyl alkyl phosphites have been found to react with cyanuric chloride to give alkyl halides and 2, 4, 6-tris(dialkyl-phosphonato)-s-triazines of 2, 4, 6-tris (diphenylphosphonato)-s-triazines. Triphenylphosphite reacts with cyanuric chloride to form triphenyl cyanurate and diphenylphosphorochloridite, $(PhO)_2PCl$. Improved methods of synthesis of 2, 4, 6-tris(diphenylphosphino)-s-triazine have been investigated and the trisulphide and triselenide have been prepared. Cyanuric chloride reacts with N,N-diethylaniline to give 2, 4-dichloro-6-N-ethylanilino-s-triazine and 2, 4-dichloro-6-p-N,N-diethylanilino-s-triazine. The compounds tris(trimethylsilyl)amine, bis(trimethylsilyl)-triphenylsilylamine, dimethylchlorosilylbis(trimethylsilyl)amine, diethylchlorosilylbis(trimethylsilyl)amine, and diphenylchlorosilylbis(trimethylsilyl)amine have been prepared from reactions of hexamethyldisilazyllithium.

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SECTION I

PHOSPHORUS DERIVATIVES OF s-TRIAZINES

A. DISCUSSION

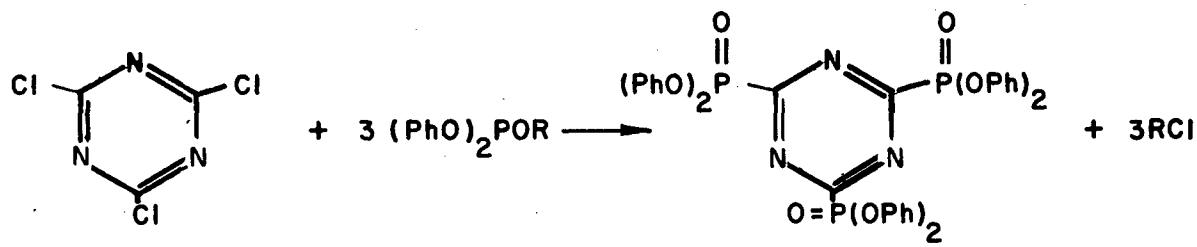
1. The Arbuzov Reaction

The first annual report (Reference 1) gave a discussion of the Arbuzov reaction between cyanuric chloride and trialkylphosphites. This section is concerned with an extension of the reaction to higher alkylphosphites and other phosphorus (III) esters. Lower trialkylphosphites and cyanuric chloride form well characterised solid trisphosphonates with sharp melting points.

With alkyl groups higher than ethyl, the products are poorly characterised oils. These compounds, unlike the lower alkyl phosphonates, are unstable and decomposition takes place on standing in air. The instability (hydrolytic and/or oxidative) may be due to the different physical nature of these compounds. This difference led us to investigate the purity of the phosphites by gas-liquid chromatography. Tri-i-propyl and tri-n-butyl phosphites were obtained commercially and distilled twice before use. In both cases, a small band was observed after the main fraction, but this appears to be an artifact formed on the column, and the area of the band is reduced at lower temperatures. It is concluded that the higher alkyl tris-phosphonates are oils unstable to atmospheric hydrolysis and thermal decomposition.

It is shown in Section IB that triphenylphosphite reacts with cyanuric chloride to form triphenyl cyanurate and the compound $(PhO)_2PCl$), although the work of Landauer and Rydon (Reference 6) has shown that the Arbuzov reaction occurs between triphenylphosphite and alkyl halides. It was considered that diphenyl alkylphosphites would give the desired tris(phenylphosphonates), and this was confirmed by experiment.

Two diphenyl alkylphosphites were prepared and reaction with cyanuric chloride gave tris(diphenylphosphonates) (I).

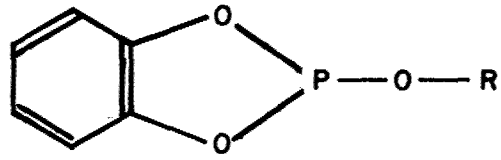


Arbuzov (Reference 2) and his co-workers have shown that the reactivity of diphenyl alkylphosphites, $(Ph0)_2POEt$, is much lower than that of trialkylphosphites. Only the methyl and ethyl esters react smoothly with alkyl iodides and higher esters undergo decomposition before reaction. The results of the present study are in accord with this observation.

With cyanuric chloride, diphenyl methylphosphite in a concentrated solution in boiling benzene reacts smoothly with evolution of 80 percent of the required methyl chloride, and formation of 2,4,6 – tris(diphenylphosphonato)-s-triazine (I, Ar = Ph), a colourless crystalline solid, stable under nitrogen but rapidly decomposed in air. This instability is similar to that of higher alkyl compounds, but was unexpected in phenyl esters of phosphonic acids. The course of the decomposition is not clear. Previous attempts to prepare the same compound

from diphenyl ethylphosphte gave 55 percent of the required ethyl chloride, but isolation of the compound was not achieved.

The interaction of o-phenylene alkylphosphites (II, R = Me, Et) and cyanuric chloride was studied.



(II)

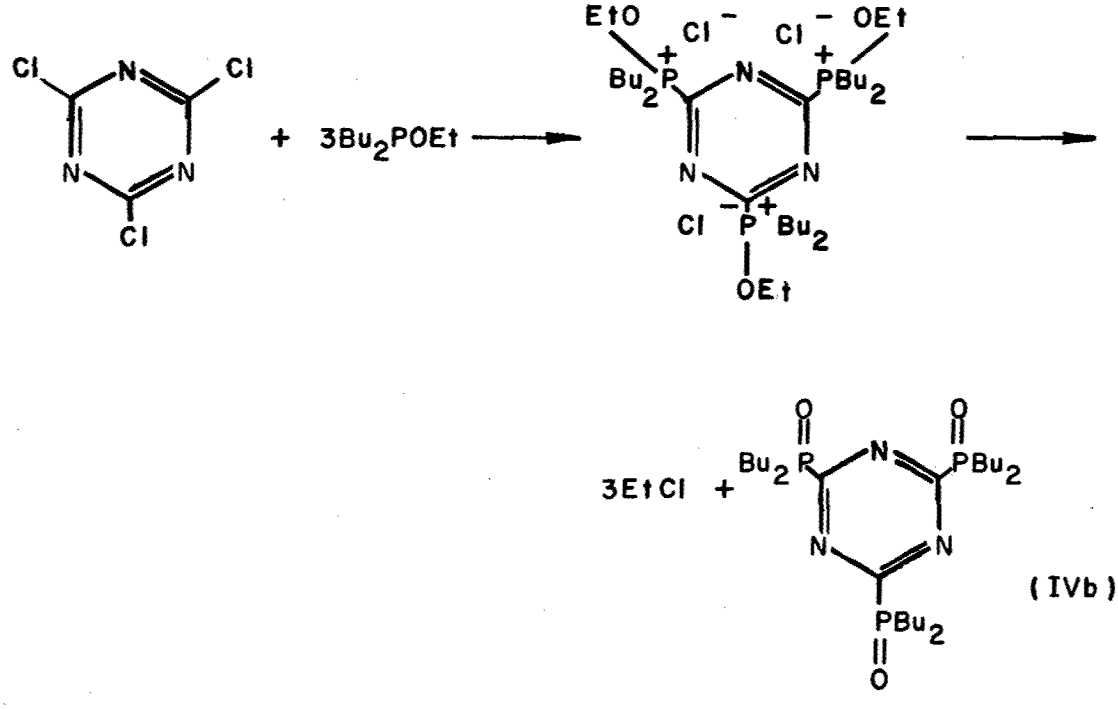
Resulting phosphonates might be expected to have a higher degree of stability than the phenyl ester, but under a variety of conditions neither of these compounds eliminated alkyl chloride before charring and decomposition occurred. Starting materials were recovered.

Two phosphinites (III) have been synthesised in order to

$$R_2POEt$$

(III) (a) R = Et
(b) R = Bu

prepare tris(phosphine oxides) (IV). Ethyl dibutylphosphinite (IIIb) and cyanuric chloride (3:1 molar ratio) in benzene gave a 56 percent yield of compound (IVb). Reaction proceeds readily with the initial formation of a crystalline solid which decomposes with evolution of ethyl chloride on heating. The solid is presumably the expected quasi-phosphonium intermediate.



(IVb)

Partially substituted phosphonatochloro-triazines were not isolated but a derivative of 2-(diethylphosphonato)-4,6-dichloro-s-triazine was prepared. (Reference 1) Other partially substituted triazine phosphonates have been synthesised by using diphenylchloro-s-triazine and phenyldichloro-s-triazine in Arbuzov reactions with lower trialkylphosphites. The reactivity is lower than that of cyanuric chloride, but only moderate conditions are required to form the corresponding phosphonates listed below. These compounds are crystalline solids which are stable in air, (c.f. trisphosphonato derivatives of s-triazine).

$Ph_2C_3N_3PO(OMe)_2$	m.p. 125-126°C.
$Ph_2C_3N_3PO(OEt)_2$	m.p. 98-99.5°C.
$PhC_3N_3[PO(OMe)_2]_2$	m.p. 113-115°C.

Properties of trisphosphonato-s-triazines

Atmospheric Hydrolysis

The esters are susceptible to atmospheric hydrolysis in varying degrees. The methyl and ethyl compounds decompose very slowly in air. The higher alkyl compounds, which are oils, form gummy decomposition products of uncertain composition during periods of a few days. The phenyl ester decomposes quickly in air, and must be recrystallised under nitrogen.

A sample of the ethyl ester was allowed to stand in air for three months. From the mixture of products a well defined crystalline solid has been isolated. Analysis indicates the loss of one ethyl group and suggests the formation of 2,4-bis-(diethylphosphonato)-6-(ethylphosphonato)-s-triazine. The infrared spectrum differs from that of the original compound in a few respects which are not explained.

Dealkylation

(a) Hydrolysis

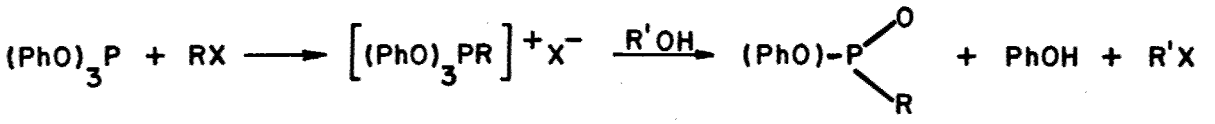
Attempts to prepare the parent acid by hydrolysis of alkyl esters were described in the first Annual Report. It is apparent that these phosphonates resemble acyl phosphonates, which have been successfully hydrolysed to acyl phosphonic acids with dry HCl in inert solvents, (Reference 3). This method was attempted, and a number of products were obtained. These were amorphous solids, insoluble in organic solvents, and none were well characterised. Analysis indicates loss of phosphorus as well as alkyl groups. It is not certain whether the triazine ring is intact.

(b) Reactions with thiourea

Thiourea forms adducts with dialkyl hydrogen phosphonates (References 4 and 5) and trialkylphosphates, (Reference 5), and an alkyl group is removed from the phosphorus ester in salt formation. This reaction has been extended to phosphonates and phosphinates, and it is shown to be a general reaction of esters of phosphorus (V) acids. Phosphonato-s-triazine esters give adducts with thiourea in poor yields. The products are hygroscopic and the method was not pursued as a synthetic route to dealkylated products.

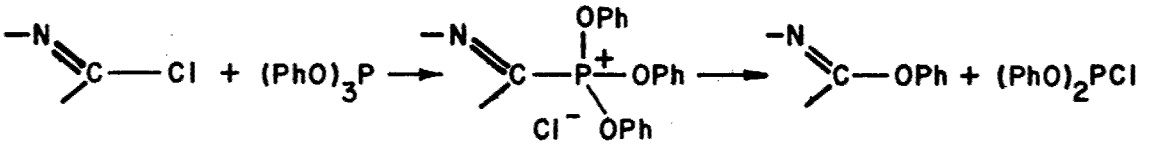
2. The Reaction of Triphenylphosphite with Cyanuric Chloride and other Acid Chlorides

Landauer and Rydon (Reference 6) have shown that the quasi-phosphonium salts, formed by reaction of triphenylphosphite with alkyl halides, interact with alcohols to form diphenylalkylphosphonates.



It was considered that triphenylphosphite and cyanuric chloride might form a similar intermediate which on treatment with an alcohol should furnish 2,4,6-tris(diphenylphosphonato)-s-triazine (I, Ar = Ph). It was shown however that the interaction of triphenylphosphite and cyanuric chloride at temperature in excess of 200°C proceeded via group exchange, with the formation of triphenyl cyanurate and diphenylchlorophosphite.

No evidence for the quasi-phosphonium salt was found, but by analogy with alkyl halides it is reasonable to suppose the reaction proceeded through this intermediate.



This reaction is similar to that of triphenylphosphite with phosphorus trichloride (Reference 7) and boron trichloride, (Reference 8) but differs from the reaction with alkyl halides (References 6 and 9) and acid chlorides of sulphur acids, (Reference 10). It would be expected that reaction of triphenylphosphite with organic acid chlorides should be similar to that of cyanuric chloride. This has been established, and a good preparative route for the synthesis of diphenylchlorophosphite has resulted from this work.

Reaction conditions and yields of diphenylchlorophosphite for the acid chlorides studied in this work are shown in Table 1.

TABLE 1

Acid Chloride	Reaction Conditions	% Yield $(PhO)_2PCl$
MeCOCl	160-170°C, sealed tube 48 hr.	62
EtCOCl	100-195°C, reflux 8 hr.	62
n-PrCOCl	100-210°C reflux 20 hr.	48
PhCOCl	200-255°C, reflux 40 hr.	40.7
$C_3N_3Cl_3$	240°C, reflux in decalin 20 hr.	60.6
PCl_3	110°C, sealed tube 18 hr.	43.1

In each case the corresponding phenyl ester was isolated and characterised. The yields of diphenylchlorophosphite are lower than those of the organic esters in all cases. This is a result of random reorganization of the chlorophosphite at the high temperatures required for reaction (Reference 7).

$$RCOCl + (PhO)_3P \longrightarrow RCOOPh + (PhO)_2PCl$$

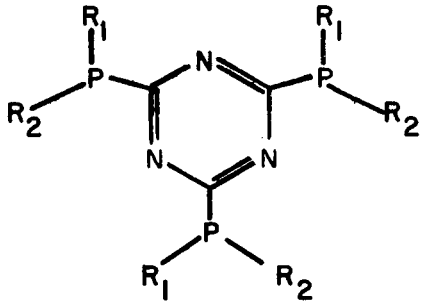
$$2(PhO)_2PCl \rightleftharpoons (PhO)_3P + PhOPCl_2, \text{ etc.}$$

3. Interaction of Trialkylphosphates with Cyanuric Chloride

Neidenzu and Dawson (Reference 11) have shown that trialkylphosphates react with B-trichloroborazole to form borazole-B-phosphates. When cyanuric chloride was dissolved in trimethylphosphate no reaction was observed, and even on boiling under reflux there was no evolution of methyl chloride. A similar result was obtained with triethylphosphate. Recovery of materials was good in both cases. Interaction of phosphates with B-trichloroborazole may be assisted by hydrogen bonding of the N-H groups but no such effect is possible in cyanuric chloride.

4. s-Triazine Phosphines

The synthesis of 2,4,6-tris(diphenylphosphino)-s-triazine (V, $R_1 = R_2 = Ph$) from cyanuric chloride and 6 moles of diphenylphosphine in benzene was described in the first annual report (Reference 1).



(V)

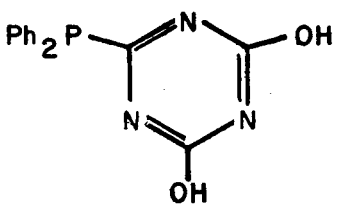
Other routes requiring only 3 moles of diphenylphosphine have been investigated as the availability of diphenylphosphine was the limiting factor in these investigations.

Reaction of diphenylphosphine (3 moles) with cyanuric chloride in aqueous suspension

This reaction was based on the successful aqueous acetone, or dioxan, method employed by e.g. Thurston et al. for the preparation of aminotriazines (Reference 12). Sodium hydroxide was used to neutralize hydrogen chloride formed. The triphosphine (V, $R_1 = R_2 = Ph$) was obtained in 65 percent yield by this method.

Reaction of diphenylphosphine (3 moles) with cyanuric chloride in xylene

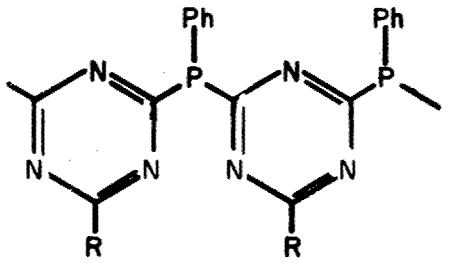
When diphenylphosphine reacted with cyanuric chloride in xylene in the presence of potassium carbonate, the major product was an amorphous hygroscopic solid containing hydroxyl groups, probably a partially substituted derivative of type (VI) or its tautomers. Only a trace of the required compound was obtained.



(VI)

Reaction of bromo-magnesium diphenylphosphide (3 moles) with cyanuric chloride

It was reported that metal diphenylphosphides Ph_2PM (M = Li, Na) did not yield the triphosphine (V) and this was considered to be caused by cleavage of the triazine ring by the highly polar reactants (Reference 1). The less polar Ph_2PMgBr was expected to be a sufficiently mild reagent to give the required product as Grignard reagents react with cyanuric chloride to give reasonable yields of alkyl and aryl triazines. But reaction proceeded as with the lithium and sodium derivatives, and a red tar was formed. The failure of this reaction to yield the required trisphosphine is difficult to interpret in the light of a recent report by Bloomfield (Reference 25) that bis(bromo-magnesium) phenylphosphide, $(BrMg)_2PPh$, reacts with dichloro triazines to form polymers of the (VII).



(VII)

Reaction of diphenylmethylphosphine (3 moles) with cyanuric chloride

Tertiary amines have been shown to react with cyanuric chloride by elimination of alkyl chloride. An attempt was made to prepare a quaternary trisphosphonium salt which might decompose on heating to the required trisphosphine. When cyanuric chloride and diphenyl-methylphosphine were heated in a 1:3 molar ratio there was no evolution of methyl chloride up to a temperature of 170°C, when considerable charring occurred. The scope of this reaction has not been investigated fully, but it appears that quaternisation does occur since no cyanuric chloride could be sublimed from the reaction mixture.

Reaction of phenylphosphine

An attempt to prepare 2,4,6-tris(phenylphosphino)-s-triazine (V, R_1 = H, R_2 = Ph) from phenylphosphine and cyanuric chloride resulted in the liberation of 60 percent of the hydrogen chloride required for complete replacement of chlorine. An intractible oil and an amorphous, apparently polymeric solid were obtained.

Properties of 2,4,6-tris(diphenylphosphino-s-triazine)

In addition to the derivatives reported previously (Reference 1), the sulphur and selenium adducts have been prepared. These are not more stable than the triphosphine to thermal decomposition. Reaction of the trisphosphine with methyl iodide does not give the expected phosphonium iodide, but cleavage of the carbon-phosphorus bond (to the triazine ring) occurs with the formation of diphenyldimethylphosphonium iodide, $[\ Ph_2PMe_2\ ]^+I^-$. No nitrogen-containing compound was identified.

Conclusions

The stability of phosphorus-carbon bonds on the s-triazine nucleus appears to be lower than when attached to an aromatic residue. A probable explanation is that cyanuric chloride should be regarded as a cyclic acid halide (Reference 26) rather than a halogenated aromatic compound. The great reactivity of cyanuric chloride (and acetyl chloride and benzoyl chloride) towards nucleophilic reagents can be contrasted with low reactivity of 1,3,5-trichlorobenzene.

B. EXPERIMENTAL

1. The Arbuzov Reaction

Preparations and reactions of the phosphorus intermediates were carried out in an atmosphere of dry nitrogen.

Intermediates

Tri-isopropylphosphite and tri-n-butylphosphite, obtained commercially, were distilled through a 50 cm. helix-packed column. $P(O\text{-}i\text{-}Pr)_3$, b.p. 59.5-60°C/8 mm. $P(O\text{-}n\text{-}Bu)_3$ b.p. 87-88°C/1.3 mm.

Diphenyl methylphosphite, b.p. 112-118°/1.5 mm., lit. (Reference 2) 165.5-166.5°/12 mm., was prepared by the method of Arbuzov and Nesterov (Reference 2) from diphenyl chlorophosphite (see section IB), methanol, and diethyl aniline in ether. Diphenyl ethylphosphite, b.p. 126-133°/0.8 mm., Lit. (Reference 2) 182-183°/17.5 mm., was prepared by a similar method. o-Phenylene methylphosphite, b.p. 82-83°/12 mm. Lit. (Reference 15) 73°/8 mm., was prepared from o-phenylene chlorophosphite, (Reference 14) methanol, and diethyl aniline in ether. o-Phenylene ethylphosphite, b.p. 90-92°/12 mm. Lit. (Reference 15) 86°/11 mm., was prepared similarly. Ethyl diethylphosphinite was obtained by the reaction of diethylchlorophosphine (Reference 16) with ethanol and diethylaniline in ether, b.p. 84-88°/12 mm. Lit. (Reference 17) b.p. 80-85°/15 mm. Ethyl di-n-butylphosphinite was prepared similarly from dibutylchlorophosphine. (Reference 13) b.p. 97-98°/12 mm., Lit.(Reference 17) 112-116°/15 mm.

2,4,6-tris(di-isopropylphosphonato)-s-triazine

Tri-isopropylphosphite (15.6 g., 3 mols) was added dropwise during 15 minutes to cyanuric chloride (4.6 g., 1 mol) cooled in ice-water. On warming to room temperature a vigorous reaction started. This was moderated by intermittent cooling and the reaction was complete after warming in a bath at 50°C for 10 mins. The condensate was collected and identified as isopropyl chloride, b.p. 36-37°C (4.7 g., 82%). The residual oil was soluble in common organic solvents, and apparently insoluble in water, with which it reacted slowly. Purification was attempted by cooling a solution of the oil in light petroleum to -78°C. There was no crystallisation after 48 hrs. A sample decomposed before distillation at ca. 135°C/0.01 mm. In air the straw-coloured oil formed a waxy solid over a period of two days. This was insoluble in non polar solvents, soluble in water, and melted with decomposition over the range 215-307°C.

2,4,6-tris(di-n-butylphosphonato)-s-triazine

Tri-n-butylphosphite (18.8 g., 3 mols) was added dropwise to boiling petroleum (100 ml.) (b.p. 100-120°), containing cyanuric chloride (4.6 g., 1 mol). The liquid collected in an

attached Dean and Stark distillation head was identified as n-butyl chloride, b.p. 78-80°C (6.3 g., 92%). Cold crystallization of the residual straw coloured was attempted from a number of solvents. Distillation gave 2.01 g. of a clear liquid, b.p. 57-59°C/0.06 mm., n_D^{20} 1.4309. Literature values for dibutyl butylphosphonate are: b.p. 160-162°C/0.06mm, (extrapolates to about 60°/0.06 mm.); n_D^{25} 1.4302. The residual product could not be distilled or sublimed without decomposition. In air it behaved like the isopropyl ester.

2,4,6-tris(diphenylphosphonato)-s-triazine

Diphenyl methyl phosphite

A solution of cyanuric chloride (4.61 g., 1 mol) in dry benzene (20 ml.) was treated with a solution of diphenyl methylphosphite (18.6 g., 3 mols) in benzene (20 ml.). The resulting solution was boiled under reflux, and the progress of the reaction was observed by noting the volume of methyl chloride collected in a trap. Condensation started after 20 minutes and continued for 7-1/2 hours when a total of 2.8 ml. (75%) was collected at -78°C. Treatment of the cooled reaction mixture with petrol (b.p. 40-60°) caused the separation of an oil which solidified on standing and trituration with petrol. The solid recrystallized from a benzene-petrol mixture to give coloruless needles, m.p. 91-94°C. Repeated crystallization gave the pure ester, m.p. 94-95°C, (13.6 g., 70%). (Found: C, 59.4; H. 3.8; N, 5.3; P, 12.4. $C_{39}H_{30}N_3O_9P_3$ requires: C, 60.2; H, 3.9; N, 5.5; P, 12.0%).

Attempts to recrystallise the product in air resulted in the formation of an oil which solidified on standing to give an amorphous powder insoluble in organic solvents, m.p. 267°C (decomp.).

When the reaction was repeated using only 20 ml. of benzene a 75 percent yield was obtained, and methyl chloride evolution was complete in 2 hours.

Diphenyl ethyl phosphite

Cyanuric chloride (6.1 g., 1 mol) and diphenyl ethyl phosphite (26 g., 3 mols) in dry benzene (70 ml.) were heated gently to boiling under reflux. After about 30 minutes ethyl chloride was evolved and collected in a graduated trap. After 4 hours no increase in volume of ethyl chloride occurred (3.1 ml., 55%). Heating was continued for a further two hours. Evaporation of benzene left a yellow oil, which was triturated with 4 x 50 ml. of petrol (b.p. 40-60°), to remove any starting materials. Crystallization was attempted by slow addition of petrol to a benzene solution but oils were formed each time this was carried out. Various attempts to separate the components on silica gel by chromatography in air using samples of ca. 0.5 g. gave no crystalline fractions. Low temperature crystallization, sublimation, and standing over a number of the usual organic solvents failed to yield any solid products.

2,4-bis(dimethylphosphonato)-6-phenyl-s-triazine

2,4-dichloro-6-phenyl-s-triazine (Reference 18) (4.52 g., 1 mol) and trimethylphosphite (6.0 g., 2.2 mol) were heated without solvent at 125-140° for 1 hour. The total volume of methyl chloride evolved (1.6 ml.) represented an 80 percent yield. The cooled reaction mixture was crystallised by trituration with light petroleum. The compound was stable in air, and was purified by repeated recrystallisation from cyclohexane-benzene to give soft colourless needles, m. p. 114-116°.

2-Dimethylphosphonato-4,6-diphenyl-s-triazine

This compound was prepared similarly from 2-chloro-4,6-diphenyl-s-triazine (Reference 18) as colourless plates, recrystallised from cyclohexane, m.p. 125-126°C (81 %). (Found: C, 59.6; H, 4.6; N, 12.5; P, 9.3. $C_{17}H_{16}N_3O_3P$ requires: C, 59.8; H, 4.7; N. 12.3; P, 9.1%).

2-Diethylphosphonato-4,6-diphenyl-s-triazine

This compound was prepared similarly from triethylphosphite as large needles, recrystallized from light petroleum, m.p. 98-99.5°C. (Found: C, 61.7; H. 5.4; N, 11.4; P, 8.5. $C_{19}H_{20}N_3O_3P$ requires C, 61.8; H, 5.5; N, 11.4; P. 8.4%). 74 percent yield.

2,4,6-tris(dibutylphosphinoxy)-s-triazine

Cyanuric chloride (4.6 g., 1 mol) in dry benzene (50 ml.) was treated dropwise at room temperature with ethyl dibutyl phosphinite (14.2 g., 3 mols). A slight yellow colour developed but no ethyl chloride was evolved and the reaction mixture temperature rose to 32°C. On heating, ethyl chloride was evolved rapidly at a bath temperature of 65°. The reaction was completed by boiling with benzene under reflux for 1 hour. A total of 3.9 ml. (90%) of ethyl chloride was collected. On cooling an oil separated, which on trituration with petrol gave a waxy solid. Recrystallization from benzene and "Analar" acetone gave small plates 7.85 g. (56%), m.p. 239-241°C. (Found: C, 57.7; H, 9.35; N, 7.6; P, 16.8. $C_{27}H_{54}N_3O_3P_3$ requires C, 57.7; H, 9.7; N, 7.5; P, 16.5%).

Reactions of o-Phenylene alkyl phosphites with Cyanuric Chloride

o-Phenylene ethyl phosphite

Cyanuric chloride (4.6 g.) and o-phenylene ethyl phosphite (14.0 g., 3 moles) were heated without solvent in a bath at 120°C. Cyanuric chloride began to sublime, and no ethyl chloride was evolved. Dry xylene (15 ml.) was added, and the reaction mixture was heated for 12 hours so that the xylene washed back any sublimed cyanuric chloride. No ethyl chloride was collected in the trap.

The reaction mixture was dark brown, and an appreciable quantity of charred solid was formed. The mixture was cooled, and the charred residue was extracted with petrol (b.p. 40-60°) (50 ml.). The filtrate was exaporated under vacuum to yield an oil, which when heated at 1 mm. in a bath at 80°C gave a sublimate of cyanuric chloride (3.2 g., 72%). Distillation of the residue gave o-phenylene ethyl phosphite (6.3 g., 45%). The still-pot residue amounted to 4.3 g. of an oily semi-solid.

Methyl Ester

It was expected that the methyl ester would undergo an Arbuzov reaction more readily. Cyanuric chloride (3.7 g., 1 mol) and o-phenylene methyl phosphite (10.2 g., 3 mols) in boiling benzene (8 ml.) gave no methyl chloride after 4 hours. An amorphous solid (0.14 g.) was filtered off after cooling, and the solution was evaporated to an oil, which resisted attempts at crystallisation. The oil, dissolved in 50 percent benzene-petrol, was treated with piperidine (10.2 g., 6 mols) dissolved in the same solvent. Piperidine hydrochloride was precipitated. The filtrate is under investigation.

Atmospheric hydrolysis of 2,4,6-tris(diethylphosphonato)-s-triazine

A sample of ester left in contact with air for three months turned pale yellow. Extraction with boiling benzene left a residue (A). The filtrate deposited colourless needles, (B) m.p. 129-135°, which when recrystallised five times from benzene had m.p. 135.5-136.5°. (Found: C, 33.1; H, 6.35; N, 8.5; P, 20.1. $C_{13}H_{26}N_3O_9P_3$ requires C, 33.8; H, 5.7; N, 9.1; P, 20.15%). Evaporation of the mother liquor gave sticky crystals (C) which when recrystallised from benzene-cyclohexane had m.p. 94-96°, and was undepressed on mixing with the original ester.

There are two bands in the infrared spectrum of compound (B) which are unexplained by the difference in structure arising from the hydrolysis of one ethyl group of the hexa-ethyl ester.

The residue (A) was soluble in water and acetic acid. Recrystallisation from aqueous acetone gave an amorphous solid, m.p. 275-280° (decomp.). (Found: C, 20.3; H, 4.8; N, 19.4; P, 20.1%, suggesting empirical formula $C_5H_{17}N_4O_7P_2$).

Reaction of 2,4,6-tris(diethyl phosphonato)-s-triazine with dry HCl

Dry HCl in a stream of nitrogen was passed through the ester (10.9 g., 1 mol) in boiling toluene (50 ml.). Ethyl chloride was evolved (5.3 ml. 61%). A clear viscous oil separated from the toluene layer. No further reaction was apparent after 24 hrs. The oil was taken up in boiling ethanol, cooled and treated with ethyl acetate. An amorphous solid slowly separated, m.p. 283-287° (decomp.). The solid was no longer soluble in ethanol. It was washed with ethanol, benzene, ethyl acetate and ether. (Found: C, 16.5; H,4.9; N, 19.7; P, 20.9%, suggesting empirical formula $C_4H_{14}N_4O_7P_2$). It appears that the triazine ring is cleaved in this product.

Reactions with Thiourea

There was no reaction between 2,4,6-tris(diethyl phosphonato)-s-triazine and thiourea on heating in a sealed tube without solvent.

In ethanol an adduct was obtained. The ester (4.9 g., 1 mol) and thiourea (2.3 g., 3 mols) were dissolved in dry ethanol (20 ml.) and heated in a sealed tube at 100°C for 4 hours. On cooling, a mass of oily crystals separated. The adduct was twice recrystallized from ethanol as colourless hygroscopic needles, m.p. 280-281° (decomp.) (2.7 g., 37.5%).

The adduct with 2,4,6-tris(dimethyl phosphonato)-s-triazine was prepared similarly by reaction of the ester (4.05 g., 1 mol) with thiourea (2.3 g., 3 mols) in methanol (20 ml.). It crystallized from methanol as hygroscopic colourless small plates, m.p. 266-267° (decomp.) (2.35 g., 35%).

2. Reaction of Triphenylphosphite with Cyanuric Chloride and Acyl Chlorides

Reaction of triphenylphosphite with cyanuric chloride

Cyanuric chloride (2.3 g., 1 mol) and triphenylphosphite (11.7 g., 3 mol) were heated in redistilled decalin (5 ml.) to 240°C (bath temperature 260°C) for 20 hours. On cooling, a solid mass of long fine needles formed. The mixture was extracted with dry ether (4 x 25 ml.) and the solid was recrystallized twice from benzene, m.p. 235-237°C. Lit. (Reference 19) m.p. 235-236° for triphenyl cyanurate. (Found: C,70.7; H, 4.5; N, 11.7. Calc. for $C_{21}H_{15}N_3O_3$: C, 70.6; H, 4.2; N, 11.8%). Yield 3.85 g., (86.5%).

After removal of ether, and decalin, the residue was distilled under vacuum to give two fractions: (a) b.p. 55-65°/2 mm., (2.21 g.) impure phenyldichlorophosphite, contaminated with decalin; and (b) b.p. 158-168°/2 mm. diphenylchlorophosphite (5.73 g., 60.6%). Lit. values in this pressure range are conflicting: Gottleib (Reference 20), b.p. 165-174°/1 mm.; Noack (Reference 21), b.p. 172°/11 mm. This product was characterised as the sulphur addition derivative, diphenylphosphorochloridothionate ($\left[(PhO)_2\overset{\overset{S}{\|}}{P}Cl \right]$, b.p. 124-126°/0.01 mm., m.p. and mixed m.p. 64-66°C. The distillation residue gave a further 0.14 g. of triphenyl cyanurate, total yield 3.99 g. (89.6%).

In another experiment, after heating a solution of triphenyl phosphite (23.3 g., 3 mol) with cyanuric chloride (4.61 g., 1 mol) in benzene (20 ml.), and boiling under reflux for 20 hr., the solution had a strong odour of cyanuric chloride. Vacuum sublimation of the residue after removal of benzene gave cyanuric chloride (4.37 g., 94.9%). Distillation gave a small forerun which contained no chlorine, and triphenylphosphite (21.2 g., 91%), b.p. 160-172°/1 mm.

A high boiling solvent, such as dekalin, is necessary for the reaction, since on heating a mixture of cyanuric chloride and triphenylphosphite without solvent, the cyanuric chloride sublimes before reaction occurs.

Reaction of triphenylphosphite with acyl chlorides

(a) Acetyl chloride

Triphenylphosphite (31.0 g., 1 mol) and redistilled acetyl chloride (9.8 g., 1.25 mol) were heated in a sealed tube to 160-170° for 48 hours. After removal of unreacted acetyl chloride (0.5 g.) the following fractions were obtained on vacuum distillation: (a) b.p. 40-42°/1.5 mm. (19.53 g.); (b) b.p. 108-110°/0.7 mm. (15.70 g.); (c) b.p. 110-160°/0.7-0.5 mm. (2.10 g.).

Fraction (a) could not be distilled at atmospheric pressure because of excessive frothing. It was dissolved in ether, washed with saturated bicarbonate solution until no more CO_2 was evolved (to destroy the phenyldichlorophosphite), and with water (4x25 ml.). The ether layer was dried overnight ($CaCl_2$) and after removal of ether, distillation gave phenyl acetate, b.p. 194-196°C (9.77 g., 71.8%), n_D^{20} 1.5028. Lit. (Reference 22) b.p. 196°C, n_D^{20} 1.5088.

Fraction (b), diphenylchlorophosphite (15.70 g., 62%), n_D^{25} 1.5773, authentic sample n_D^{25} 1.5776, (Found: Cl, 13.8. Calc. for $C_{12}H_{10}ClO_2P$: Cl, 14.0%), was further characterised by the preparation of the sulphur derivative, m.p. 64-67°C, mixed authentic sample, m.p. 64-66.5°C.

Fraction (c) was mainly triphenylphosphite contaminated with diphenylchlorophosphite.

Acetyl chloride and triphenylphosphite (same quantities as before) were recovered almost quantitatively after boiling the mixture under reflux at atmospheric pressure for 48 hr.

(b) Benzoyl chloride

Triphenylphosphite (31.0 g., 1 mol) and benzoyl chloride (15.0 g., 1.07 mol) were boiled under reflux for 40 hr. The bath temperature was raised to 255° to maintain boiling as the reaction progressed. Distillation at 10 mm. gave benzoyl chloride (2.50 g.). The residue was

fractionated under vacuum on a spinning band column: (a) 6 fractions, b.p. 130-134.5°/3 mm. (22.13 g.); (b) 3 fractions, b.p. 185.5-186°, diphenylchlorophosphite, (10.25 g., 40.7%), n_D^{25} 1.5775. This gave $(PhO)_2P(S)Cl$, identical with an authentic sample.

Fractions (a) solidified on cooling and gave positive tests for P and Cl. The higher boiling fractions were increasingly oily. Since the phenylbenzoate could not be freed from the by-product, phenyldichlorophosphite, even by spinning band fractionation, the whole was treated as before (see phenyl acetate) to give phenylbenzoate (17.6 g., 88%, m.p. 70-71°C (from 90% ethanol), undepressed by admixture with an authentic sample.

(c) Propionyl chloride

The reaction was carried out as for benzoyl chloride, using triphenylphosphite (310 g.) and propionyl chloride (92.5 g., 1 mole). After 8 hours, when the bath temperature had been raised to 195°C, boiling ceased. The following fractions were obtained by distillation: (a) b.p. 50-65°/2 mm., $PhOPCl_2$ and $C_2H_5CO_2Ph$ (142 g.); (b) b.p. 133-136°/2 mm., $(PhO)_2PCl$ (157 g., 62%), n_D^{25} 1.5780. The higher boiling residue, $(PhO)_3P$, was not distilled.

(d) Butyryl chloride

The reaction was carried out similarly using triphenylphosphite (31 g.) and butyryl chloride (10.7 g.). After 20 hr., when the bath temperature was 210°C, the reaction mixture was cooled. Distillation gave three fractions: (a) b.p. 52-57°/0.7 mm., $PhOPCl_2$ and $C_3H_7CO_2Ph$ (17.6 g.); (b) b.p. 110-120°/0.6-0.5 mm., $(PhO)_2PCl$ (12.1 g., 48%); (c) b.p. 120-160°/0.5 mm., crude $(PhO)_3P$ (5.1 g.).

Similar quantities of these reactants were also heated in a sealed tube at 180° for 5 hr. A 62% yield of $(PhO)_2PCl$ (13.1 g.) was obtained.

Reaction of triphenylphosphite with phosphorus trichloride

Triphenylphosphite (62 g., 2 mol) and phosphorus trichloride (13.7 g., 1 mol) were heated in a sealed tube at 110°C for 18 hr. (Conant et al. (Reference 7) used a temperature of 150°C for 8 hr.). This experiment was attempted to find whether a better yield of diphenylchlorophosphite could be obtained at lower reaction temperature. On distillation the mixture gave the following fractions: (a) b.p. 60-61°/1.5 mm., $PhOPCl_2$ (11.74 g., 10%), n_D^{25} 1.5608; (b) b.p. 61-134°/1.5 mm., forerun, 2.70 g.; (c) b.p. 132-133°/1.2 mm., $(PhO)_2PCl$ (32.58 g., 43.1%). n_D^{25} 1.5776; (d) mainly b.p. 168-178°/ 0.9 mm., $(PhO)_3P$ (18.44 g., 29.7%), n_D^{25} 1.5853. Redistillation of diphenylchlorophosphite, taking the fraction b.p. 110-114°/0.8 mm., gave no change of refractive index.

Preparation of diphenylphosphorochloridothionate $\left[(PhO)_2P(S)Cl \right]$

Gottleib's method (Reference 20) was used to prepare this compound. An equimolar mixture of diphenylchlorophosphite and thiophosphoryl chloride were heated at 120° for one hour. Phosphorus trichloride was distilled, and the residue, which solidified on cooling, was distilled

in vacuo, b.p. 124-127°/0.01 mm. It was purified by vacuum sublimation (80-90°/0.1 mm.), m.p. 64-66°C. This compound was used for mixed melting point determinations in the characterisation of diphenylchlorophosphite.

3. Interaction of Trialkylphosphates with Cyanuric Chloride

Trimethyl phosphate (21 g., 3 mols) was added to cyanuric chloride (9.2 g., 1 mol). The mixture was heated for 1 hour to a temperature of 230°C, and the phosphate was kept boiling under reflux. There was no condensate in the trap during this period. Distillation of the mixture gave trimethyl phosphate (18.1 g., 86.2%). Recrystallisation of the residue from carbon tetrachloride gave cyanuric chloride (7.5 g., 81.5%).

With triethyl phosphate no ethyl chloride was evolved and the starting materials were recovered: triethyl phosphate 79.3 percent; cyanuric chloride 84 percent.

4. s-Triazine Phosphines

Diphenylphosphine was prepared by the cleavage of triphenylphosphine with sodium (2 moles) in liquid ammonia and hydrolysis of the reaction mixture with oxygen-free water (Reference 23). Phenylphosphine was obtained from phenyl dichlorophosphine by the method of Mann and Millar (Reference 24). Diphenyl methylphosphine was prepared from sodium diphenylphosphide and methyl iodide in liquid ammonia (Reference 23).

Preparation of 2,4,6-tris(diphenylphosphino)-s-triazine

Aqueous suspension method

A solution of cyanuric chloride (6.1 g., 1 mole) in acetone (50 ml.) was added to ice water (ca. 100 g.) with stirring. Diphenylphosphine (18.6 g., 3 moles) in acetone (20 ml.) was added dropwise during 15 mins. A pale green colour appeared, and remained throughout the reaction. On complete addition the reaction mixture was heated to 100°C for 30 minutes, cooled, and neutralised with dilute sodium hydroxide solution. The reaction mixture was investigated in air.

A sticky green mass, insoluble in the aqueous phase was formed: on extraction with benzene all the coloured component was taken up in the organic layer, which was then filtered to remove a small amount of yellow solid. The benzene solution was evaporated, and the residue triturated with methanol which removed most of the green colour. Recrystallisation from benzene-alcohol (charcoal) gave a very pale green solid, m.p. 138-140°C, undepressed by admixture with an authentic sample of 2,4,6-tris(diphenylphosphino)-s-triazine. Yield 13.7 g. (65%). The pale green colour could be removed from a sample by passing a benzene solution through a short column of unactivated silica gel.

Potassium carbonate in xylene method (unsuccessful)

A solution of diphenylphosphine (18.6 g., 3 moles) in xylene (30 ml.) was added dropwise to a stirred solution of cyanuric chloride (6.1 g., 1 mole) in xylene (100 ml.) at room temperature. A slightly oily precipitate was formed. On heating to 50-60°C hydrogen chloride gas was evolved, which was titrated continuously against standard alkali; a total of 1.05 mole was evolved and an oily precipitate was formed. After 2 hours, when the evolution of gas had ceased, potassium carbonate (8.6 g.) was added in ca. 1 g. quantities. After stirring for 20 minutes the mixture was washed with cold boiled water (2x100 ml.). The yellow oily precipitate was still present, and did not dissolve on the addition of benzene (40 ml.). (The required product is very soluble in benzene). The reaction mixture was then treated with ethanol

(20 ml.) and the oily solid dissolved. The organic layer was filtered* and evaporated to an oil, which solidified on trituration with petrol. It was taken up in ethanol and precipitated with benzene to give a very hygroscopic pale yellow solid. It was too sticky to put into a melting point tube, and on the Kofler block it formed an oil before melting. The infrared spectrum showed the presence of phenyl groups (690, 730 $cm.^{-1}$) and bands similar to those of cyanuric acid (strong peaks at 1610 and 1440 $cm.^{-1}$). The product gave positive tests for P and N, a negative Cl test, and is probably a hydroxy phosphino triazine.

Magnesium bromodiphenylphosphide method (unsuccessful)

Diphenylphosphine (9.3 g., 3 moles) in benzene (30 ml.) was added dropwise to a stirred Grignard solution prepared from magnesium (1.2 g.) and bromobenzene (8 g.) in 150 ml. ether. The phosphine-Grignard reagent started to crystallise out, and a further 25 ml. of benzene was added. The solution was stirred very rapidly and cooled in an acetone-solid CO_2 bath. A solution of cyanuric chloride (3 g., 1 mole) in 50 percent benzene-ether (20 ml.) was added dropwise. A red colouration appeared immediately. On complete addition a viscous red-brown oil was present. The mixture was hydrolysed with 10 percent aqueous ammonium chloride, and the organic layer which separated was treated with sufficient benzene to dissolve the oil, and evaporated to remove ether. The benzene solution was filtered, and petrol (b.p. 40-60°) was added slowly. A floculant precipitate formed immediately, but on settling this reformed a red-brown tarry oil. Elementary analysis showed the presence of N, P, Mg (trace), and Cl. The product was similar to those obtained from the sodium and lithium reactions.

Reaction of diphenyl methylphosphine (3 mols) with cyanuric chloride

Cyanuric chloride (2.3 g., 1 mol) and diphenyl methylphosphine (7.1 g., 3 mols) were mixed at room temperature and heated slowly to 100°C. The solid did not dissolve, but darkened to a yellow-brown colour, and no volatile gases were condensed in a trap at -78°C. The temperature was raised to 170°C during 2 hours. At this temperature the solid charred rapidly with no evidence of methyl chloride elimination. The residue from extraction with cold benzene, a black tarry mass, was subjected to vacuum sublimation (bath temperature 90°C/0.1 mm.). No cyanuric chloride was recovered. The tarry solid dissolves, apparently with decomposition, in hydroxylic solvents. The experiment is to be repeated using an inert solvent.

Reaction of phenyl phosphine with cyanuric chloride

Phenyl phosphine (16.5 g., 3 mols) in benzene (100 mls.) was added to cyanuric chloride (9.2 g., 1 mol) in benzene (150 ml.) during 30 minutes. An oily solid settled very slowly. When the mixture was heated to boiling under reflux, the oily solid settled more quickly. Hydrogen chloride was liberated, and the progress of the reaction was followed by continuous titration against standard alkali. Reaction ceased after 72 hours (60.3% of HCl). The supernatant liquor was evaporated to give an amorphous solid, insoluble in benzene and common organic solvents. With water it decomposed, giving the unmistakable odour of phenyl phosphine. Elements present were C, H, N, P and Cl (trace).

The oil was very hygroscopic, and even with rigorous precaution to maintain an inert atmosphere it could not be crystallised. Elements present were C, H, P, Cl and N (trace). The method was discarded in favour of aqueous suspension technique.

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*the residue (ca. 100 mg.) gave 35 mg. of the required product.

Reactions of 2,4,6-tris(diphenyl phosphino)-s-triazine

Addition of sulphur

Sulphur (0.10 g., 3 mols) and the triphosphine (0.63 g., 1 mol) were heated in benzene (20 ml.) boiling under reflux for 2-1/2 hours. The product, recrystallised twice from benzene, was a mass of fine pale yellow needles, m.p. 223-225°C, (0.64 g., 90%). (Found: C, 64-45; H, 4.4; N, 6.2; P, 13.8; S, 13.2. $C_{39}H_{30}N_3P_3S_3$ requires: C, 64.2; H, 4.1; N, 5.8; P, 12.7; S, 13.2%).

Addition of selenium

Redistilled selenium (0.12 g.) reacted similarly with the triphosphine (0.32 g.). Recrystallisation from benzene gave orange cubes of the triselenide, m.p. 232-234°C, (0.27 g., 57%). (Found: P, 10.4. $C_{39}H_{30}N_3P_3Se_3$ requires: P, 10.7%).

Reaction with methyl iodide

A solution of the triphosphine (3.17 g.) in boiling benzene (15 ml.) was treated with methyl iodide (4 ml.) and methanol (1 ml.). An oil settled from the boiling solution after 30 minutes, and solidification occurred on cooling. Extraction with boiling methanol and addition of ether gave colourless needles of dimethyl diphenyl phosphonium iodide, m.p. 250-251°. (Found: C, 49.3; H, 5.0; P, 8.7. Calc. for $C_{14}H_{10}PI$: C, 49.1; H, 4.7; P, 9.05%). It was further characterised by preparation of the picrate, m.p. 119-121°. (Found: C, 53.8; H, 4.25; N, 9.3; P, 7.0. $C_{20}H_{18}N_3O_7P$ requires: C, 54.2; H, 4.1: N, 9.5: P,7.0). The iodide had an undepressed melting point when mixed with an authentic sample of dimethyl diphenyl phosphonium iodide.

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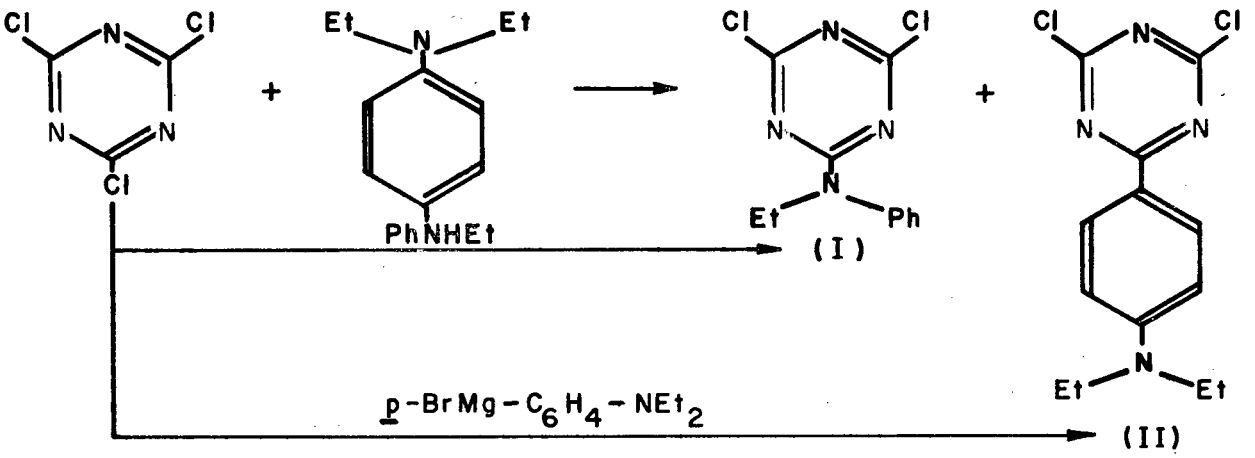
SECTION II

NITROGEN DERIVATIVES OF s-TRIAZINE

A. DISCUSSION

The behaviour of N,N diethylaniline was investigated as a possible hydrogen halide-acceptor for reactions involving cyanuric chloride and non-metallic hydrides. Replacement of the chlorine atoms of cyanuric chloride by primary and secondary amines has been studied extensively (Reference 1), but reactions with tertiary bases have been neglected. Saure (Reference 2) investigated the reaction of cyanuric chloride with aqueous pyridine, but no reaction was observed with anhydrous pyridine, even on boiling. It is also reported (Reference 3) that cyanuric chloride reacts with a mixture of diphenylamine and triethylamine in toluene to give ethyl chloride and 2-chloro-4-diethylamino-6-N,N-diphenylamino-s-triazine.

Cyanuric chloride and N,N-diethylaniline in 1:2 mole ratio were heated together for an hour at 125°C. Ethyl chloride was evolved and N,N-diethylaniline hydrochloride was isolated from the reaction mixture. Two derivatives of s-triazine were obtained: 2,4-dichloro-6-N-ethylanilino-s-triazine (I), a colourless crystalline solid, m.p. 116.5-117°C; and 2,4-dichloro-6-p-N,N-diethylanilino-s-triazine (II), a yellow crystalline solid, m.p. 157-157.5°C, which gave intensely fluorescent solutions in hydrocarbon solvents. The structures were confirmed by independent synthesis. The N-ethyl derivative (I) was prepared from cyanuric chloride and N-ethylaniline by the method of Thurston et al., (Reference 4) and the N,N-diethyl derivative (II) was prepared from cyanuric chloride and the Grignard reagent of p-bromo-NN-diethylaniline.



The infrared spectra of the compounds in potassium bromide discs were examined. 2,4-Dichloro-6-N-ethylanilino-s-triazine (I) absorbed strongly at 1570, 1475, 1325, 1225, 1180, 1105, 843, 808, 793, 768, 760, and 697 cm.$^{-1}$, and 2,4-dichloro-6-p-N,N- diethylanilino-s-triazine (II) absorbed strongly at 1615, 1520, 1415, 1355, 1275, 1232, 1192, 1105, 967, 843, 798, and 719 cm.$^{-1}$

The dealkylation reaction is analogous to the reaction between trimethylamine and hexachlorocyclotriphosphazatriene (Reference 5), and other similarities between the s-triazine and phosphazene systems have been reported recently (Reference 6).

B. EXPERIMENTAL

Cyanuric chloride (18.5 g., 0.1 mole) and N,N-diethylaniline (29.8 g., 0.2 mole) were heated at 125°C in the absence of solvent for one hour, when evolution of ethyl chloride ceased. Addition of benzene gave an insoluble brown solid which was purified by sublimation at 100°C/2 mm. and identified as N,N-diethylaniline hydrochloride (5.1 g., 0.027 mole), m.p. 158-159°C. Evaporation of the filtrate and sublimation at 100-120°C/0.01 mm. gave a yellow solid (24.2 g.) from which colourless crystals of 2,4-dichloro-6-N-ethylanilino-s-triazine (I) (10.1 g., 37%), m.p. 116.5-117°C, (Found: C, 49.4; H, 4.0; Cl, 26.0; N, 20.9. $C_{11}H_{10}Cl_2N_4$ requires: C, 49.1; H, 3.8; Cl, 26.4; N, 20.8%) and yellow crystals of 2,4-dichloro-6-p-N,N-diethylanilino-s-triazine (II) (6.4 g., 21%), m.p. 157-157.5°C, (Found: C,52.3; H, 5.1; Cl, 23.7; N, 18.4. $C_{13}H_{14}Cl_2N_4$ requires C, 52.5; H, 4.8; Cl, 23.9; N, 18.9%) were obtained by fractional crystallisation from light petroleum (b.p. 60-80°C).

N-Ethylaniline was added slowly to a cooled suspension of cyanuric chloride (18.5 g.) and sodium carbonate (10.6 g.) in aqueous acetone. Extraction with light petroleum gave 2,4-dichloro-6-N-ethylanilino-s-triazine (16.0 g., 60%), m.p. and mixed m.p. with (I) 116.5-117°C, whose identity was confirmed by analysis and infrared spectroscopy. p-N,N-Diethylaniline magnesium bromide, prepared from p-bromo-N,N-diethylaniline (11.4 g., 0.05 mole) and magnesium (1.3 g.) in tetrahydrofuran (70 ml.) was added to a solution of cyanuric chloride (7.4 g., 0.04 mole) in tetrahydrofuran (50 ml.). The mixture was boiled under reflux (1/2 hour) and after removal of solvent, the benzene-soluble material was eluted with benzene on a silica gel chromatography column. Recrystallisation of the product from light petroleum gave 2,4-dichloro-6-p-N,N-diethylanilino-s-triazine (3,8 g., 30%), m.p. and mixed m.p. with (II) 157-157.5°C, whose identity was confirmed by analysis and infrared spectroscopy.

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SECTION III

REACTIONS OF HEXAMETHYLDISILAZYLLITHIUM

A. DISCUSSION

The action of ammonia on trimethylchlorosilane has been reported by Sauer (Reference 1) to yield only hexamethyldisilazane and no primary or tertiary silylamine. Shaw and co-workers (Reference 2) have shown that it is possible to prepare tristrimethylsilylamine, $N(SiMe_3)_3$, from n-butyllithium and hexamethyldisilazane by reaction of the resulting hexamethyldisilazyllithium, $(Me_3Si)_2NLi$, with trimethylchlorosilane. Wannagat (Reference 3) has also described the preparation of tristrimethylsilylamine from hexamethyldisilazyllithium and trimethylchlorosilane in a sealed tube at 100-150°C. The compound has also been prepared recently by Goubeau (Reference 5) from reaction of the sodium compound of hexamethyldisilazane with trimethylchlorosilane in xylene.

This compound has been prepared in a substantially increased yield and bis(trimethylsilyl)triphenylsilylamine(Reference 2) has also been prepared and purified. It was reported previously (Reference 4) that triphenylchlorosilane does not react with hexamethyldisilazyllithium.

The synthesis of these compounds takes place in three stages: (a) the synthesis of hexamethyldisilazane from trimethylchlorosilane and ammonia:

$$2Me_3SiCl + 3NH_3 \longrightarrow (Me_3Si)_2NH + 2NH_4Cl$$

(b) conversion of hexamethyldisilazane to hexamethyldisilazyllithium by the action of n-butyllithium:

$$(Me_3Si)_2NH + BuLi \longrightarrow (Me_3Si)_2NLi + B_4H_{10}$$

(c) reaction of hexamethyldisilazyllithium with the chloro compound.

$$(Me_3Si)_2NLi + R_3SiCl \longrightarrow (Me_3Si)_2NSiR_3 + LiCl$$

The compounds, dimethylchlorosilylbis(trimethylsilyl)amine, diethylchlorosilylbis(trimethylsilyl)amine, and diphenylchlorosilylbis(trimethylsilyl)amine, were prepared from hexamethyldisilazyllithium by similar methods.

B. EXPERIMENTAL

Preparation of hexamethyldisilazane

The method of Sauer (Reference 1) was used to prepare hexamethyldisilazane. A solution of trimethylchlorosilane (130 ml.) in dry ether (500 ml.) was placed in a one litre flask fitted with a reflux condenser and an inlet for the addition of gaseous ammonia. The rapid addition of ammonia was continued for 3 hours, after which the mixture was boiled gently under reflux by means of an I.R. lamp for one hour. The hexamethyldisilazane solution in ether was separated from the ammonium chloride by filtration through a sintered disc under anhydrous oxygen-free conditions. The ether solution was distilled fractionally and the fraction having a b.p. 124-126°C was retained. The refractive index was n_D^{20} 1.4066

instead of n_D^{20} 1.4078, the value of pure hexamethyldisilazane. Gas-liquid chromatography showed the existence of two distinct peaks and the hexamethyldisilazane was redistilled on a spinning band column. Fractions boiling between 125°C and 126.5°C gave single peaks on the G.L.C. apparatus.

Preparation of n-butyllithium

The preparation of n-butyllithium in n-pentane was based on the method of Gilman.(Reference 6).

A three-neck 250 ml. flask was equipped with a stirrer, reflux condenser, addition funnel and a nitrogen inlet. When the apparatus was completely dry and all the air had been displaced by nitrogen, 80 ml. of pentane and 5 g. of lithium metal, wired and cut into small pieces, were added to the flask. A solution of n-butyl chloride (37 ml.) in 50 ml. of n-pentane was added slowly to the lithium-n-pentane mixture (1 drop/sec.) by means of the dropping funnel. After a 10-minute induction period, the reaction warmed up and a blue precipitate appeared in the flask. When the addition of n-butyl chloride was complete (3 hr.), the mixture was boiled by means of an I.R. lamp for 2 hours. On cooling to room temperature the mixture was filtered under anhydrous and oxygen-free conditions through a glass tube packed with glass wool and into a dropping funnel. A 2 ml. sample of the n-pentane solution was hydrolysed and titrated with HCl to determine n-butyllithium content. The yield was 62.5 percent.

Synthesis of tristrimethylsilylamine

The apparatus was set up as before, and air was blown out of the dry apparatus by a stream of dry nitrogen. Hexamethyldisilazane (0.1 mole plus 10% excess) was dissolved in 50 ml. of light petroleum (b.p. 60-80°). n-Butyllithium solution (0.1 mole) was added dropwise with stirring and the reaction mixture became yellow. The reaction mixture was boiled under reflux for 30 minutes by the aid of an I.R. lamp.

Trimethylchlorosilane (0.11 mole, 14 ml.) dissolved in 25 ml. of dry THF was added to hexamethyldisilazyllithium (0.1 mole) in a dry flask. An exothermic reaction took place and chloride precipitated. Stirring was continued for two hours and the mixture was boiled under reflux for another eight hours. The pale yellow supernatant solution was filtered off under anhydrous oxygen-free conditions. The filtrate was evaporated to dryness under reduced pressure and the residue redissolved in light petroleum (b.p. 60-80°). The insoluble lithium chloride was removed by filtration (94%). The petroleum solution was evaporated slowly under reduced pressure and the residue was heated under vacuum at 42°/0.01 mm. to give a sublimate of tristrimethylsilylamine (28%), m.p. and mixed m.p. 67-68°C.

Reaction of hexamethyldisilazyllithium with triphenylchlorosilane

Hexamethyldisilazyllithium prepared as before, reacted with triphenylchlorosilane dissolved in THF (125 ml.). The mixture was boiled under reflux for 10 hours. Lithium chloride was removed by filtration. The solvents, n-pentane and THF, were evaporated from the reaction mixture under vacuum and the residue redissolved incompletely in benzene. The filtrate was evaporated to reduce the volume and the crystals obtained from this solution sublimed at 130-140°C/0.15 mm. to give triphenylsilylbis(trimethylsilyl)amine (21%), m.p. and mixed m.p. 112°C.

Reaction of hexamethyldisilazyllithium with dimethyldichlorosilane (1:1 molar ratio)

Hexamethyldisilazyllithium was prepared as before. A solution of dimethyldichlorosilane (7.9 ml., 0.61 mole) in 25 ml. of dry THF was placed in a flask, and a solution of hexamethyl-

disilazyllithium (0.61 mole) in THF and pentane was added at the rate of one drop per second. The mixture was boiled under reflux for 8 hours. Fine crystals of lithium chloride (96%) were removed by filtration under anhydrous oxygen-free conditions. The filtrate was evaporated to dryness and redissolved incompletely in light petroleum (b.p. 60-80°). The filtrate was evaporated to about 20 ml. and left in the ice-box overnight but no crystals were formed. Heating under vacuum (68°C/0.1 mm.) gave a white crystalline sublimate of dimethylchlorosilylbis(trimethylsilyl)amine, $(Me_3Si)_2NSiMe_2Cl$, (21%), m.p. 43-45°C. (Found: C, 37.8; H, 9.5; Cl, 15.1; N, 6.3. $C_8H_{24}ClNSi_3$ requires C, 37.9; H, 9.5; Cl, 14.0; N, 5.5%).

Reaction of hexamethyldisilazyllithium with dimethylchlorosilane (2:1 molar ratio)

A solution of hexamethyldisilazyllithium (0.06 mole) in THF and pentane was placed in a flask, and dimethyldichlorosilane (0.03 mole) in dry THF (25 ml.) was added dropwise with stirring. The mixture was boiled under reflux for 12 hours. Lithium chloride (94%) was removed by filtration under anhydrous oxygen-free conditions. The solvents were evaporated and the residue redissolved incompletely in light petroleum (b.p. 60-80°). The filtrate was evaporated to reduce the volume and was left in the ice-box overnight, but no crystals were obtained. Heating in vacuum (68°/0.1 mm.) gave a colourless crystalline sublimate of dimethylchlorosilylbis(trimethylsilyl)amine, $(Me_3Si)_2NSiMe_2Cl$, 16%), m.p. and mixed m.p. 43-45°C.

Reaction of hexamethyldisilazyllithium with diethyldichlorosilane (1:1 molar ratio)

Hexamethyldisilazyllithium was prepared as before and a solution (0.5 mole) in THF and pentane was placed in a flask. Diethyldichlorosilane (0.5 mole) in dry THF (25 ml.) was added with stirring, at the rate of about one drop per second. The mixture was boiled under reflux for 24 hours. Fine crystals of lithium chloride were removed by filtration under dry oxygen-free conditions.

$$(Me_3Si)_2NLi + Et_2SiCl_2 \longrightarrow (Me_3Si)_2NSiEt_2Cl + LiCl$$

The filtrate was evaporated to dryness and extracted with light petroleum. The remaining insoluble lithium chloride was filtered off (total 90%) and the filtrate evaporated to a volume of about 20 ml. No crystals were obtained from this solution which was evaporated under vacuum. On heating (80°C/0.05 mm.) a white sublimate appeared on the cold parts of the apparatus. This was identified as diethylchlorosilylbis(trimethylsilyl)amine, $(Me_3Si)_2NSiEt_2Cl$, (21%), m.p. 83-85°C. (Found: C, 42.7; H, 9.95; Cl, 13.25; N, 5.0; Si, 28.9. $C_{10}H_{28}ClNSi_3$ requires: C, 42.6; H, 9.94; Cl, 12.6; N, 5.0; Si, 29.8%).

Reaction of hexamethyldisilazyllithium with diphenyldichlorosilane (1:1 molar ratio)

Hexamethyldisilazyllithium (0.4 mole) reacted similarly with diphenyldichlorosilane (0.4 mole). Lithium chloride was removed by filtration and the filtrate was evaporated to dryness and extracted with dry benzene. Evaporation of the solvent and distillation at 120°C/0.01 mm. gave a product which solidified on cooling. This was purified by sublimation to give colourless crystals of diphenylchlorosilylbis(trimethylsilyl)amine, $(Me_3Si)_2NSiPh_2Cl$,(20%), m.p. 53-55° C.

$$(Me_3Si)_2NLi + Ph_2SiCl_2 \longrightarrow (Me_3Si)_2NSiPh_2Cl + LiCl$$

(Found: C, 56.8; H, 7.0; Cl, 10.0; N, 3.9; Si, 20.8%; M, 389. $C_{18}H_{28}ClNSi_3$ requires: C, 57.2; H, 7.4; Cl, 9.4; N, 3.7; Si, 22.2%; M, 378).

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Reactions of cyanuric chloride with trialkyl phosphites, diphenyl alkyl phosphites, triphenyl phosphite and diethylaniline are reported. Preparations and properties of 2, 4, 6-tris(diphenylphosphino)-s-triazine have been investigated. New derivatives of hexamethyldisilazyl-lithium have been prepared.

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